An equation of state from cool-dense fluids to hot gases for mixed elements

G. Q. Luo [1]

Yunnan Observatory, Kunming, 650011, P.R. China
Beijing astronomical observatory, Beijing, 100080, P.R. China

ABSTRACT

An equation of state for the domain extending from hot gases to cool-dense fluids is formulated for a hydrogen-helium mixture. The physical processes take account of temperature ionization and dissociation, electron degeneracy, Coulomb coupling and pressure ionization. Pressure ionization and Coulomb coupling are studied with simple and comprehensive modeling. A single and complete algorithm is achieved with explicit expressions available for the whole domain from hot gases to cool dense fluids $(T > 10^2 \mathrm{K})$. Pressure ionization and Coulomb coupling have been examined for their contributions to the pressure and internal energy. The result reveals that their contributions smooth the variation of the pressure and internal energy in the region of pressure ionization even at very low temperatures.

Subject headings: atomic processes, equation of state, stars: low mass, planets

1.   Introduction

The equation of state (EOS) of cool dense fluids is concerned with the interiors of very low mass stars, brown dwarfs and giant planets in astrophysics. The complexity of the physical processes of such an EOS stems from the inclusion of interparticle interactions among atoms, molecules, ions and electrons. The physical processes concerned mainly include two types, i.e. pressure ionization and Coulomb coupling. Many studies have been carried on for Coulomb coupling among charged particle. For instance, the internal energy of fully ionized plasmas of classical one-component has been given by advanced physics models (see Slattery and Doolen 1980) for the case of strong coupling. The free energy of fully ionized hydrogen-helium mixture has also been evaluated for thermodynamic properties with strong coupling (see DeWitt and Hubbard 1976). The Coulomb coupling in weak limits can be well described by Debye-Huckel model (see Cox and Giuli 1968; Mihalas et al. 1988). However, the Coulomb coupling between strong and weak limits still remains for the study of its model and effects. In addition, the problem of pressure ionization has been remaining thorny in the EOS calculation for cool dense fluids (see Saumon et al. 1995). Although the advanced physical models of pressure ionization have been studied for the EOS (see Blenski and Ishikawa 1995; Saumon and Chabrier 1991, 1992), it is not easy to incorporate them into the astrophysical EOS for their practical use and investigation. In this paper, we establish the physical models for pressure ionization and Coulomb coupling which have simple expressions and can be easily incorporated into the EOS formalism.

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[1]Postdoctor, Beijing astronomical observatory.

Almost all of the EOS for cool dense fluids are given with their results in tabular form for astrophysical application (e.g. Fontain et al. 1977; Magni and Mazzitelli 1979; Mihalas et al. 1988; Saumon et al. 1995). This is because the complex formalism and time-consuming calculation of the EOS for cool dense fluids stem from many physical processes. They include temperature dissociation and ionization, electron degeneracy, Coulomb coupling and pressure ionization, etc. However, explicit and simplified expressions for a comprehensive EOS can be of benefit to the study of the unfamiliar physical processes concerned in the EOS and to the study of their importance to and influences on astrophysical phenomena. We aim to present such an algorithm for the EOS covering the domain from cool dense fluids to hot gases.

Furthermore, it is also important to assure the reliability for the formulated EOS and its results. Therefore, we not only establish the explicit and simple expressions for the EOS but also compare the resulted EOS with those from other more sophisticated models. In order to preserve the continuity and generality of the EOS, we formulate the EOS on the basis of the grand canonical approach in the chemical picture for the EOS (see Luo 1994). It allows to establish a single algorithm of the EOS available for the whole domain from cool dense fluids to hot gases, even when many physical processes are taken into account. The grand canonical approach in the chemical picture also allows to include mixed elements in the EOS. The EOS presented in this paper is formulated for a hydrogen(H)-helium(He) mixture and takes into account the physical processes of atomic ionization, molecular dissociation, electron degeneracy, Coulomb coupling, pressure ionization, etc.

In Sect.2 we establish the models of pressure ionization and Coulomb coupling. Sect.3 presents an algorithm of calculating thermal equilibrium. The algorithm of calculating the pressure and internal energy is presented in Sect. 4. In Sect. 5, the calculated results of the EOS are compared with other EOS, and are examined for the contributions of pressure ionization and Coulomb coupling to thermodynamic functions.

2. Pressure ionization and Coulomb coupling

We start from a H-He mixture gas with mass density ρ, temperature T and the mass abundances X and Y for H and He. In a volume V, the number of nuclei of H and He are given by

$$N_{\mathrm{H}} = N_{\mathrm{A}}\rho V X/A_{\mathrm{H}}, \qquad N_{\mathrm{He}} = N_{\mathrm{A}}\rho V Y/A_{\mathrm{He}}, \tag{1}$$

with the Avagadro's number N_{A}, the atomic weights $A_{\mathrm{H}} = 1.0079$ and $A_{\mathrm{He}} = 4.0026$.

Two physical processes, i.e., Coulomb coupling of charged particles and pressure ionization of atoms, have been taken into account for the nonideal effects on the EOS. Owing to the complexity of such physical processes, their incorporation into the EOS requires some assumptions to allow simplified and approximate models.

2.1. Coulomb coupling

The Coulomb coupling has considerable influences on the EOS, especially in fully ionized plasmas. In partially ionized fluids, it plays a subtle role in the determination of the ionization degrees as well as thermodynamic quantities. We first approximate the Coulomb coupling by a one-component model of fully ionized plasmas, and then add the corrections of partial ionization and mixed elements to its formalism.

The Coulomb coupling can well be described in two limit cases, i.e., weak coupling ($\Gamma \ll 1$) and strong coupling ($\Gamma \gg 1$). The Coulomb coupling parameter $\Gamma = (Ze)^2/\bar{r}kT$ is defined by the nuclear charge Z, the ion sphere radius $\bar{r}$ and temperature T. For a H-He mixture, we define the average nuclear charge Z as

$$Z = \frac{N_{\mathrm{H}} + 2N_{\mathrm{He}}}{N_{\mathrm{H}} + N_{\mathrm{He}}}. \tag{2}$$

The ion sphere radius $\bar{r}$ is determined by the number of ions N_{ion} in the volume V using the approximation $(4\pi/3)\bar{r}^3 N_{\mathrm{ion}}/V = 1$. Considering the correction from the partial ionization, we approximate the ion number by $N_{\mathrm{ion}} = N_{\mathrm{e}}/Z$ with the number of free electrons N_{e}. As a result, the Coulomb coupling parameter can be written as

$$\Gamma = \frac{(Ze)^2}{kT}\left(\frac{4\pi N_{\mathrm{e}}}{3ZV}\right)^{1/3} \tag{3}$$

with the corrections from the partial ionization and mixed elements.

In the case of strong coupling ($\Gamma \gg 1$), the energy of a fully ionized plasma with one component (of nuclear charge Z) is found to be

$$E_{\mathrm{cc}} = -kTN_{\mathrm{ion}} \times 0.89752\Gamma, \qquad (\Gamma \gg 1) \tag{4}$$

with the ion number N_{ion} (see Slattery et al. 1980). For weak coupling $\Gamma \ll 1$, the Debye-Hückel model can be used to obtain its Coulomb coupling energy (see Cox & Giuli 1968). We ignore the effect of electron degeneracy and suppose a fully ionized plasma with one component (of nuclear charge Z). We thus have

$$E_{\mathrm{cc}} = -kTN_{\mathrm{ion}} \times (3/4)^{1/2}\left[(1 + 1/Z)\,\Gamma\right]^{3/2}, \qquad (\Gamma \ll 1). \tag{5}$$

The results for both the limit cases indicate that the Coulomb coupling energy per ion in unit kT (i.e. $E_{\mathrm{cc}}/N_{\mathrm{ion}}kT$) is a function of the Coulomb coupling parameter Γ and the nuclei charge Z. The functions ($E_{\mathrm{cc}}/N_{\mathrm{ion}}kT$) of the two limit cases for $Z = 1$ are plotted versus Γ in Fig. 1 which shows their intersection at $\Gamma = 0.13$.

In our EOS formalism the average potential energy of each free electron from Coulomb coupling ϵ_{cc} is adopted. The internal energy from the Coulomb coupling is calculated in terms of

$$E_{\mathrm{cc}} = N_{\mathrm{e}}\epsilon_{\mathrm{cc}} - N_{\mathrm{e}}\left(\frac{\partial \epsilon_{\mathrm{cc}}}{\partial \ln T}\right)_{VN} \tag{6}$$

which is the result of the EOS with the grand canonical approach in the chemical picture (see Luo 1994, 1996). With this definition and the constraints of the results of Coulomb coupling energy in two limit cases, the average energy of each free electron from Coulomb coupling can be fitted to be

$$\epsilon_{\mathrm{cc}} = -kT\frac{g(\Gamma, Z)}{Z} \tag{7}$$

with a fitting function $g(\Gamma, Z)$ defined by

$$\begin{aligned}
1/g &= 1/g_1 + 1/g_2 , \\
g_1 &= (2/3)(3/4)^{1/2}(1 + 1/Z)^{3/2}\Gamma^{3/2} , \\
g_2 &= 0.89752\Gamma .
\end{aligned} \tag{8}$$

The internal energy from Coulomb coupling resulted from the fitting function is therefore given by

$$E_{\rm cc}(\Gamma, Z) = -kTN_{\rm ion} \times g(\Gamma, Z) \left(\frac{\partial \ln g}{\partial \ln \Gamma} \right).$$ (9)

according to Eqs. (3), (6) and (7). It has asymptotic form as in equation (4) for strong coupling case and as equation (5) for weak coupling case. The results from equation (9) for the Coulomb coupling energy per ion in unit kT ($E_{\rm cc}/N_{\rm ion}kT$) with $Z = 1$ are plotted in Fig. 1. It is compared with the results of the two limit cases. The accurate results for $\Gamma \geq 0.3$ (see Slattery and Doolen 1980) are also plotted in Fig. 1. They indicate that the simply fitted formula still overestimate the Coulomb coupling energy about tens percent in the intermediate range of Γ. However, it is easy to add the power weighting to the fitting formulae to obtain better fitted results.

Fig. 1.— The fitting function for logarithmic ($E/kTN_{\rm ion}$) versus logarithmic Γ (solid line) , with those of the weak Coloumb coulping $\Gamma \ll 1$ (dotted line) and of the strong Coloumb coupling $\Gamma \gg 1$ (dashed line), and with the accurate results for $\Gamma > 0.3$ (circles) given by Slattery and Doolen (1980).

The fitted formula of equation (7) has a derivative with respect to $\ln \Gamma$

$$\frac{\partial \ln g}{\partial \ln \Gamma} = \frac{5}{2} - \frac{(3/2)g_1 + g_2}{g_1 + g_2} \ ,$$ (10)

with the functions g_1 and g_2 defined in equation (8). It has asymptotic values $3/2$ for $\Gamma \ll 1$ and 1 for $\Gamma \gg 1$. It will be used in Sect.4 for calculating the pressure and internal energy from Coulomb coupling.

2.2. Pressure ionization

Pressure ionization is caused by the interaction of an atom with surrounding particles which is responsible for the dissolution of atomic energy states. In the gases with high temperatures (e.g. $T \geq 10^5 K$), a great fraction of free electrons and ions lead to the Stark ionization of atoms. This has been well described by the MHD EOS with the occupation probability formalism (see Hummer & Mihalas 1988). For cool dense fluids, however, neutral atoms and molecules dominate the interaction on an acted-upon atom. Accordingly, the sophisticated physical models are established to produce continuous solutions of the EOS (e.g. Saumon & Chabrier 1992; Blenski & Ishikava 1995). These models are based on the advanced physics theory and partly examined by experimental data.

For astrophysical application and research, however, we may make approximate and statistical models for the complicated physical processes of pressure ionization. This will allow to examine the uncertainty of pressure ionization and its influence on the models of astrophysical objects through the EOS.

Our model for pressure ionization is based on the energy change of an acted atom by the pressure impact of acting particles. When an acted-upon atom is collided by other particles, the pressure impact can always increase its energy. If the acted-upon atom is supposed to have an effective volume v_1, the impact by acting particles with an equivalent pressure P_1 will increase the energy of the acted-upon atom by an amount of $\Delta E_1 = P_1 v_1$. This is the result from the view of statistical mechanics. In thermodynamic equilibrium with temperature T, the energy change ΔE_1 leads to a Boltzmann factor $W = \exp(-\Delta E_1/kT)$ for the existence probability of the atom. We thus can use the resulted factor W to present the occupation probability for the specified atom.

The acting particles include all classical particle with the number of atomic neclei $N_\mathrm{H} + N_\mathrm{He}$. They also include the bound electrons of other atoms beyond the mean separation d that the acted-upon atom can feel. The mean separation of atoms d is defined by

$$\frac{4\pi}{3}d^3 \left(\frac{N_\mathrm{H} + N_\mathrm{He}}{V}\right) = 1 \tag{11}$$

for a H-He mixture with the number of atomic nuclei $N_\mathrm{H} + N_\mathrm{He}$.

Suppose the atoms of H and He have the hydrogen-like wave functions of ground states $w(Zr) = \sqrt{2}Zre^{-2Zr}$, we then have the number of the bound electrons beyond the mean separation d

$$N_\mathrm{e}^\mathrm{b} = N_\mathrm{H} \int_d^\infty w(r)\mathrm{d}r + 2N_\mathrm{He} \int_d^\infty w(2r)\mathrm{d}r = N_\mathrm{H}f(d) + 2N_\mathrm{He}f(2d), \tag{12}$$

with a function $f(x)$ defined by

$$f(x) = e^{-2x}(1 + 2x + 2x^2). \tag{13}$$

It is a rough approximation that the mean separation of atoms is used to determine the number of the acting electrons. Because an atom with a kinetic energy $(3/2)kT$ can always approach another atom closer than the mean separation d, it can feel more bound electrons of other atoms than those outside the separation d. As a result, the integration limit d in equation (12) should be corrected by taking account of the thermal motion of the atom. Nevertheless, the thermal motion of the atom play a role in the determination of the integration limit at relatively high temperatures. In that case, temperature ionization play a more important role than pressure ionization. We find that the inclusion of the thermal motion dose not have a very important effect on the model of pressure ionization in the EOS formalism. In addition, its inclusion will complicate the model of pressure ionization in the EOS formalism. We therefore do not present its formulation in this paper.

The acting atoms and ions are classical particles while the acting electrons with the number N_e^b behave like the Fermi-Dirac particles. As a result, the equivalent pressure P_1 from the acting particles is given by the Fermi-Dirac statistics

$$P_1 = kT\left(\frac{N_\mathrm{H} + N_\mathrm{He}}{V}\right) + \frac{2}{3}kT\frac{N_\mathrm{e}^\mathrm{b}}{V}\frac{F_{3/2}(\lambda_1)}{F_{1/2}(\lambda_1)} \tag{14}$$

with the Fermi-Dirac integral $F_{3/2}$ and $F_{1/2}$. The degeneracy of the acting electrons λ_1 is determined by

$$N_\mathrm{e}^\mathrm{b}/V = C_\mathrm{e}T^{3/2}F_{1/2}(\lambda_1) \tag{15}$$

with a constant $C_e = (\sqrt{2}/\pi^2)(km_e/\hbar^2)^{3/2}$ (see Luo 1994).

The effective volume v_1 of the acted-upon atom is defined by its radius r_j in terms of $v_1 = (4\pi/3)r_j^3$. As a result, we obtain the occupation probability in terms of $W = \exp(-P_1 v_1/kT)$ in a logarithmic form

$$\ln W_j = -\frac{4\pi}{3}r_j^3 \left[\frac{N_H + N_{He}}{V} + \frac{2}{3}C_e T^{3/2} F_{3/2}(\lambda_1) \right] \tag{16}$$

for an atom with an effective radius r_j. In equation (16) the first term is identical to the result of the hard sphere model of atoms (see Hummer and Mihalas 1988). The second term is the result of the interaction from the bound electrons of other atoms on the acted-upon atom. The radii of atomic hydrogen (HI) and singly ionized helium (HeII) are taken to be $r_{HI} = a_0$ and $r_{HeII} = 0.5a_0$ with the Bohr radius a_0, and that of atomic He is assumed to be $r_{HeI} = 0.8a_0$. The resulted occupation probabilities are thereby represented by W_{HI}, W_{HeI} and W_{HeII}.

The occupation probability given by equation (16) is an explicit function of T, N_H and N_{He} as well as r_j. It thus can be incorporated into the calculation of the thermal equilibrium. Its simplified form allows to obtain analytical expressions for their contribution from pressure ionization to the pressure and internal energy (see Sect. 4.5).

3. Thermal equilibrium quantities of the EOS

3.1. Thermal equilibrium quantities

Thermal equilibrium quantities are explicitly defined by the degrees of atom ionization and molecule dissociation. For the EOS in the chemical picture, the determination of thermodynamic functions significantly depends on the degrees of ionization and dissociation. According to the grand canonical approach in the chemical picture (see Luo 1994), the thermal equilibrium of a mixture can be specified by the probabilities of atomic nuclei in various configurations.

We total include six configurations for H and He. They are specified for hydrogen by molecular state H_2 (abbreviated as M), atomic state HI and ionized state HII, as well as for helium by atomic state HeI, singly ionized state HeII and doubly ionized state HeIII. The probabilities of hydrogen nuclei in the configurations H_2, HI and HII are thereby specified by x_M, x_{HI} and x_{HII}, with a normalization condition $x_M + x_{HI} + x_{HII} = 1$. The probabilities of helium nuclei in the configurations HeI, HeII and HeIII are specified by x_{HeI}, x_{HeII} and x_{HeIII} with $x_{HeI} + x_{HeII} + x_{HeIII} = 1$.

The energy of an atomic configuration is equal to the energy of bound electrons in it, and is determined by the ionization energy and dissociation energy. For hydrogen and helium, their configuration energies are defined by

$$
\begin{aligned}
E_{H_2} &= -2\chi_{HI} - \chi_{H_2} \\
E_{HI} &= -\chi_{HI} \\
E_{HII} &= 0 \\
E_{HeI} &= -\chi_{HeI} - \chi_{HeII} \\
E_{HeII} &= -\chi_{HeII} \\
E_{HeIII} &= 0
\end{aligned}
\tag{17}
$$

The energies of ionization and dissociation χ_{H_2}, χ_{HI}, χ_{HeI}, χ_{HeII} for H and He have values 4.48, 13.598, 24.587, and 54.416 in eV. The energy of a fully ionized configuration is equal to zero because

it has no bound electron. The configurational energy of H_2 specified by E_{H_2} is equal to the energy of two electrons bound in H_2.

The probabilities of atomic nuclei in various configuration are alternative quantities for describing ionization and dissociation degrees. The number of atomic nuclei in each configuration is equal to the number of atomic nuclei multiplied by the corresponding probability. The number of free electrons is thus given for a H-He mixture by

$$N_e = N_H x_{HII} + N_{He}(x_{HeII} + 2x_{HeIII}) \, . \tag{18}$$

3.2. The equation for thermal equilibrium

A H-He mixture in thermal equilibrium is described by its temperature T, volume V and the number of hydrogen nuclei N_H and that of helium nuclei N_{He}. Following the conservation equation for the electron number (see Luo 1994) we have an equation for thermal equilibrium

$$N_H + 2N_{He} = C_e T^{3/2} V F_{1/2}(\lambda - \epsilon_{cc}/kT) + N_H(x_M + x_{HI}) + N_{He}(2x_{HeI} + x_{HeII}) \tag{19}$$

with a constant $C_e = (\sqrt{2}/\pi^2)(km_e/\hbar^2)^{3/2}$ and the Fermi-Dirac integral $F_{1/2}$.

Of equation (19) the left-hand side counts the total number of electrons from hydrogen and helium while the right hand side represents the distribution of electrons in molecular, atomic, ionic and free states. On the right-hand side, the first term is the number of free electrons, the second term counts the bound electrons in molecular and atomic configurations of hydrogen, and the third term counts those in the atomic and ionic configurations of helium.

Equation (19) has an unique unknown variable which is the electron degeneracy λ. The probabilities of nuclei in various configurations x_M, x_{HI}, x_{HeI} and x_{HeII} are all its explicit functions according to Sects. 3.3 and 3.4. The Coulomb coupling energy for each free electron ϵ_{cc} is defined in Sect. 2.2. It is also an explicit function of the electron degeneracy λ by means of the free electron number N_e. As a result, the equation for thermal equilibrium, equation (19), can be solved for the electron degeneracy λ as well as other equilibrium quantities x_M, x_{HI}, x_{HeI}, x_{HeII} and N_e.

3.3. Equilibrium quantities of helium

Helium has two degrees of ionization and thus has three configurations HeI, HeII and HeIII. The probabilities of atomic nuclei in various configurations can be determined by the formalism of the atomic configuration probability (see Luo 1994). The grand partition function of electrons in an atomic configuration $|NE>$ is defined by $\mathcal{Z} = gW \exp(N\lambda - E/kT)$ with the statistical weight g, the number of bound electrons N, the configuration energy E (i.e. the energy of bound electrons) and the occupation probability W.

As a result, we have the grand partition functions for various configurations of helium

$$\begin{aligned}
\mathcal{Z}_{HeI} &= W_{HeI} \exp[2\lambda - E_{HeI}/kT] \\
\mathcal{Z}_{HeII} &= 2W_{HeII} \exp[\lambda - E_{HeII}/kT] \\
\mathcal{Z}_{HeIII} &= 1
\end{aligned} \tag{20}$$

which result from $g = 1$ and $N = 2$ for HeI and $g = 2$ and $N = 1$ for HeII. The fully ionized configuration HeIII has its grand partition function equal to unity because it has no bound electron and is characterized by $N = 0$, $E = 0$, $g = 1$ and $W_{\text{HeIII}} = 1$. The occupation probabilities W_{HI} and W_{HeI}, which account for pressure ionization, are formulated in Sect. 2.2.

The probabilities of helium nuclei in various configurations are therefore given by

$$
\begin{aligned}
x_{\text{HeI}} &= \mathcal{Z}_{\text{HeI}}/\mathcal{Z}_{\text{He}} \\
x_{\text{HeII}} &= \mathcal{Z}_{\text{HeII}}/\mathcal{Z}_{\text{He}} \\
x_{\text{HeIII}} &= \mathcal{Z}_{\text{HeIII}}/\mathcal{Z}_{\text{He}} \\
\mathcal{Z}_{\text{He}} &= \mathcal{Z}_{\text{HeI}} + \mathcal{Z}_{\text{HeII}} + \mathcal{Z}_{\text{HeIII}}
\end{aligned}
\tag{21}
$$

where $\mathcal{Z}_{\text{He}}$ is the total grand partition function of elections for He. They satisfy a normalization condition $x_{\text{HeI}} + x_{\text{HeII}} + x_{\text{HeIII}} = 1$.

3.4. Equilibrium quantities of hydrogen

We include three configurations H_2, HI and HII for hydrogen in the EOS formalism. Because of the inclusion of molecular hydrogen the formalism of the probability of hydrogen nuclei has a different form from those of helium. We first give the probabilities of hydrogen nuclei in HI and HII for which no molecular state is taken into account

$$
\begin{aligned}
y_{\text{HI}} &= \mathcal{Z}_{\text{HI}}/\mathcal{Z}_{\text{H}} \\
y_{\text{HII}} &= \mathcal{Z}_{\text{HII}}/\mathcal{Z}_{\text{H}} \\
\mathcal{Z}_{\text{H}} &= \mathcal{Z}_{\text{HI}} + \mathcal{Z}_{\text{HII}}
\end{aligned}
\tag{22}
$$

with normalization $y_{\text{HI}} + y_{\text{HII}} = 1$. The grand partition functions of electrons in HI and HII are defined by

$$
\begin{aligned}
\mathcal{Z}_{\text{HI}} &= 2W_{\text{HI}}\exp[\lambda - E_{\text{HI}}/kT] \\
\mathcal{Z}_{\text{HII}} &= 1
\end{aligned}
\tag{23}
$$

which are the results of $g = 2$ and $N = 1$ for HI, and the fully ionized configuration for HII.

When we introduce the probability of hydrogen nuclei in the molecular configuration x_{M}, the exclusion of hydrogen nuclei in the molecular configurations leads to the actual probabilities of hydrogen nuclei in configurations HI and HII

$$
\begin{aligned}
x_{\text{HI}} &= y_{\text{HI}}(1 - x_{\text{M}}) \\
x_{\text{HII}} &= y_{\text{HII}}(1 - x_{\text{M}}).
\end{aligned}
\tag{24}
$$

For the dissociation of molecular hydrogen, the pressure equilibrium constant defined by Vardya (1960) leads to

$$
K(T) = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}} = \frac{(kTN_{\text{HI}}/V)^2}{kTN_{\text{H}_2}/V} = \frac{x_{\text{HI}}^2}{x_{\text{M}}}\frac{2kTN_{\text{H}}}{V}
\tag{25}
$$

with the probabilities of hydrogen nuclei x_{M} in H_2 and x_{HI} in HI. Equation (25) has employed the number of hydrogen molecules $N_{\text{H}_2} = N_{\text{H}}x_{\text{M}}/2$ and the number of hydrogen atoms $N_{\text{HI}} = N_{\text{H}}x_{\text{HI}}$.

With the normalization conditions $x_M + x_{HI} + x_{HII} = 1$ and $y_{HI} + y_{HII} = 1$, Eqs. (24) and (25) lead to a solution for the probability of hydrogen nuclei in the molecular configuration

$$x_M = 1 + R - \sqrt{R^2 + 2R} \qquad (26)$$

with

$$R = \frac{K(T)}{4y_{HI}^2 kT(N_H/V)}. \qquad (27)$$

The Vardya's (1960) expression for the pressure equilibrium constant can be written as

$$K(T) = P_0 \exp[-(D_1/kT) + (D_2/kT)^2 - (D_3/kT)^3] \qquad (28)$$

with a pressure constant $P_0 = 3.4159 \times 10^{12} \mathrm{dyn/cm^2}$. The constants D_1, D_2 and D_3 take values 4.92516, 0.237047 and 0.148409 in eV.

Temperature ionization and pressure ionization of hydrogen atoms have fatal effects on the dissociation of molecular hydrogen. The reduction of the number of hydrogen atoms rapidly decreases the number of hydrogen molecules. In the above formalism, the decrease of y_{HI} reduces x_M in terms of $x_M \approx 1/2R$ for $R \gg 1$ according to Eqs. (26) and (27).

3.5. Thermal equilibrium calculation

We finally established an algorithm for calculating thermal equilibrium quantities from Eqs. (19)-(28). Equations (21), (24) and (26) define the probabilities of atomic nuclei in various configurations as functions of the degeneracy λ. The equation for thermal equilibrium, equation (19), therefore becomes an enclosed equation with one variable λ for which can be solved. The iteration method is an effective and fast way to solve equation (19) in most region of the $\rho - T$ domain except in the region where strong pressure ionization takes place. In contrast, the bisection method is powerful and can always arrive at unique convergent solutions in the whole $\rho - T$ domain.

The thermal equilibrium of a mixture can be well revealed by its mean molecular weights in a $\rho - T$ domain. The mean molecular weight μ is defined as the mean weight per particle in atomic mass unit, i.e. $\mu = \rho V N_A/N$ with the total number of particles N in the mixture. We thus have the mean molecular weights μ for a H-He mixture in terms of

$$\frac{1}{\mu} = \frac{X}{A_H}(1 - x_M/2 + x_{HII}) + \frac{Y}{A_{He}}(1 + x_{HeII} + 2x_{HeIII}). \qquad (29)$$

It is the result of the degrees of ionization and dissociation through the probabilities of atomic nuclei in various configurations.

We performed a calculation of thermal equilibrium for a H-He mixture with abundances $X/Y = 0.7/0.3$. The reciprocals of the resulted mean molecular weights $1/\mu$ are plotted in Fig. 2 for a $\rho - T$ domain. It shows three slopes for low densities $\log \rho < 0$ from low temperatures to high ones. They correspond to the dissociation of hydrogen molecules, the ionization of hydrogen atoms and that of helium atoms respectively. There are other three steep slopes in the density range $0 < \log \rho < 2$ for low temperatures $\log T < 5$, which are the results of pressure ionization of hydrogen atoms and helium atoms. The surface plot of Fig. 2 shows that the minimum and maximum values of $1/\mu$, 0.422 and 1.614, correspond respectively to the gases of completely neutral helium and molecular hydrogen and those of completely ionized mixture.

Fig. 2.— The reciprocals of the mean molecular weight $1/\mu$ in a $\rho - T$ domain for a H-He mixture $X/Y = 0.7/0.3$.

In addition, Fig. 2 reveals that the densities for pressure ionization of hydrogen are located between 1 to 10 g/cm^3 at very low temperatures while those of helium between 10 to 100 g/cm^3. The densities for pressure ionization are almost independent of temperatures, and pressure ionization take place in very narrow density ranges. However, we realize that the occupation probability by equation (16) is formulated especially for cool-dense fluids. Although it can produce pressure ionization for partial ionized gases at high temperatures, it underestimates the effect of pressure ionization by the Stark effect for $\log T > 4.5$.

4. Thermodynamic functions of the EOS

4.1. Pressure and internal energy

The EOS uniquely determines the pressure $P(\rho, T, X)$ and internal energy $E(\rho, T, X)$ as well as other thermodynamic quantities as functions of density ρ, temperature T and element abundance X, Y. The pressure P, the internal energy density per unit mass $E/\rho V$ and their derivatives with respect to ρ and T are required to dictate the mechanical and thermal equilibria of stars and planets. In this section, we present the comprehensive expressions for the pressure P and internal energy E as functions of T, N_{H} and N_{He} which are related with T, ρ and X by equation (1).

We include the following contributions to the pressure and internal energy: (1) the classical particle (molecules, atoms and ions) and the free electrons as Fermi-Dirac particles; (2) Coulomb coupling for P_{cc} and E_{cc}; (3) pressure ionization for P_{pi} and E_{pi}. The internal energy also include (4) the configurational terms of atoms, ions and molecules E_{conf} and (5) the vibrational and rotational terms of hydrogen molecules E_{rv}.

As a result, the pressure and internal energy for a H-He mixture is written as

$$P = kT\frac{N_{\mathrm{c}}}{V} + \frac{2}{3}kT\frac{N_{\mathrm{e}}}{V}\frac{F_{3/2}(\lambda_{\mathrm{e}})}{F_{1/2}(\lambda_{\mathrm{e}})} + P_{\mathrm{cc}} + P_{\mathrm{pi}} \tag{30}$$

$$E = \frac{3}{2}kTN_{\mathrm{c}} + kTN_{\mathrm{e}}\frac{F_{3/2}(\lambda_{\mathrm{e}})}{F_{1/2}(\lambda_{\mathrm{e}})} + E_{\mathrm{cc}} + E_{\mathrm{pi}} + E_{\mathrm{conf}} + E_{\mathrm{rv}} \tag{31}$$

with the number of the classical particles $N_c = N_H(1 - x_M/2) + N_{He}$ and the number of free electrons N_e given by equation (18). In the Fermi-Dirac integrals $F_{1/2}$ and $F_{3/2}$, the effective term of the electron degeneracy $\lambda_e = \lambda - \epsilon_{cc}/kT$ is determined by the electron degeneracy λ and the Coulomb coupling energy for the free electron ϵ_{cc}. The first and second terms in Eqs. (30) and (31) represent the ideal contributions from the classical particles and the free electrons.

4.2. Energy of configurations

The configurational energy comes from the energy of bound electrons in molecules, atoms and ions. This energy is determined by the numbers of nuclei in various configurations and the energies of various configurations are defined by equation (17). For a H-He mixture, the total energy from various configurations is given by

$$
\begin{aligned}
E_{conf} \;=\; & N_H(x_M E_{H_2}/2 + x_{HI}E_{HI} + x_{HII}E_{HII} - E_{H_2}/2) \\
+ \; & N_{He}(x_{HeI}E_{HeI} + x_{HeII}E_{HeII} + x_{HeIII}E_{HeIII} - E_{HeI})
\end{aligned}
\tag{32}
$$

The last terms in two brackets, i.e. $(-E_{H_2}/2)$ and $(-E_{HeI})$, are added to retain a zero point of the configurational energy in the case of 100% molecular hydrogen and neutral helium.

4.3. Rotational and vibrational energies of hydrogen molecules

The rotational and vibrational states of hydrogen molecules (H_2) have contribution to the internal energy. The characteristic temperature of its rotation is $\Theta_r = 85.38$K and that of its vibration is $\Theta_v = 5987$K (see Gopal 1974). For temperatures $T \gg \Theta_r$ which is our interest for cool dense fluids, the rotation of H_2 is sufficiently excited and its rotational energy reaches the classical value of kT. In contrast, the vibration of hydrogen molecules cannot be excited to classical states at temperatures $T < \Theta_v$ or $T \sim \Theta_v$. Therefore, we use the Einstein function (see Gopal 1974) for the vibrational energy of H_2.

As a result, the contribution from the rotation and vibration of H_2 to the internal energy is given by

$$
E_{rv} = kTN_{H_2} + \left[\frac{k\Theta_v}{e^{\Theta_v/T} - 1} + \frac{1}{2}k\Theta_v \right] N_{H_2}
\tag{33}
$$

with the number of hydrogen molecules $N_{H_2} = N_H x_M/2$. In equation (33) the first term results from the rotation of H_2 while the second term from its vibration. The factor E_{rv}/kTN_{H_2} is sensitive to temperatures around $T \sim \Theta_v$.

4.4. Contribution from Coulomb coupling

The contribution from Coulomb coupling to the pressure and internal energy is calculated from the Coulomb coupling energy contributed to the free electrons. Equation (7) defines the average energy from Coulomb coupling for each free electron ϵ_{cc}. According to the formalism of the EOS formulated by Luo (1994), the pressure from Coulomb coupling is given by

$$
P_{cc} = -\frac{N_e}{V} \left(\frac{\partial \epsilon_{cc}}{\partial \ln V} \right)_{TN} = \frac{N_e \epsilon_{cc}}{V} \frac{1}{3} \left(\frac{\partial \ln g}{\partial \ln \Gamma} \right)
\tag{34}
$$

and the internal energy by

$$E_{\mathrm{cc}} = N_{\mathrm{e}}\epsilon_{\mathrm{cc}} - N_{\mathrm{e}}\left(\frac{\partial \epsilon_{\mathrm{cc}}}{\partial \ln T}\right)_{VN} = N_{\mathrm{e}}\epsilon_{\mathrm{cc}}\left(\frac{\partial \ln g}{\partial \ln \Gamma}\right) \tag{35}$$

which are the results of equation (7). The derivative factor in Eqs. (34) and (35) has been given by equation (10) and is a function of the Coulomb coupling parameter Γ and the average nuclear charge Z. A relation $P_{\mathrm{cc}} = E_{\mathrm{cc}}/3V$ is retained for the Coulomb coupling from Eqs. (34) and (35).

4.5. Contribution from pressure ionization

Pressure ionization is caused by interparticle interactions and has its contributions to the pressure P and internal energy E. Its contributions have been formulated as the results of the occupation probability W of bound atomic configurations (see Luo 1994) in terms of

$$P_{\mathrm{pi}} = \frac{1}{2}\sum_j kT\frac{N_j}{V}\left(\frac{\partial \ln W_j}{\partial \ln V}\right)_{TN_j}, \tag{36}$$

$$E_{\mathrm{pi}} = \frac{1}{2}\sum_j kTN_j\left(\frac{\partial \ln W_j}{\partial \ln T}\right)_{VN_j}, \tag{37}$$

where the sums go over all bound configurations for $j = \{H_2, HI, HeI, HeII\}$ with the species number N_j. The factor $(1/2)$ is introduced to take account of the fact that the interparticle interactions responsible for pressure ionization have actually been counted twice for each atom in the summation.

The fully ionized ions, e.g. HII and HeIII, have no contribution because they have no bound systems interacting with surroundings. The contribution from molecular hydrogen should be included in that from hydrogen atoms since its pressure dissociation results from pressure ionization of atomic hydrogen according to Eqs. (26) and (27). As a result, the contribution from pressure ionization to the pressure for a H-He mixture is given by

$$
\begin{aligned}
P_{\mathrm{pi}} = &\ \frac{1}{2}kT\frac{N_{\mathrm{H}}}{V}(x_{\mathrm{M}} + x_{\mathrm{HI}})\left(\frac{\partial \ln W_{\mathrm{HI}}}{\partial \ln V}\right) \\
&+ \frac{1}{2}kT\frac{N_{\mathrm{He}}}{V}\left[x_{\mathrm{HeI}}\left(\frac{\partial \ln W_{\mathrm{HeI}}}{\partial \ln V}\right) + x_{\mathrm{HeII}}\left(\frac{\partial \ln W_{\mathrm{HeII}}}{\partial \ln V}\right)\right]
\end{aligned}
\tag{38}
$$

and that to the internal energy given by

$$
\begin{aligned}
E_{\mathrm{pi}} = &\ \frac{1}{2}kTN_{\mathrm{H}}(x_{\mathrm{M}} + x_{\mathrm{HI}})\left(\frac{\partial \ln W_{\mathrm{HI}}}{\partial \ln T}\right) \\
&+ \frac{1}{2}kTN_{\mathrm{He}}\left[x_{\mathrm{HeI}}\left(\frac{\partial \ln W_{\mathrm{HeI}}}{\partial \ln T}\right) + x_{\mathrm{HeII}}\left(\frac{\partial \ln W_{\mathrm{HeII}}}{\partial \ln T}\right)\right].
\end{aligned}
\tag{39}
$$

The derivative terms in Eqs. (38) and (39) are determined by the formalism of the occupation probability W_j. They have analytical expressions for $j = \{HI, HeI, HeII\}$

$$\left(\frac{\partial \ln W_j}{\partial \ln V}\right)_{TN_j} = \frac{4\pi}{3}r_j^3\left[\frac{N_{\mathrm{H}} + N_{\mathrm{H}}}{V} + \frac{2}{3}C_{\mathrm{e}}T^{3/2}F_{3/2}(\lambda_1)h(\lambda_1)\right] \tag{40}$$

$$\left(\frac{\partial \ln W_j}{\partial \ln T}\right)_{VN_j} = \frac{4\pi}{3}r_j^3 C_{\mathrm{e}}T^{3/2}F_{3/2}(\lambda_1)\left[h(\lambda_1) - 1\right] \tag{41}$$

as the results of equation (16). The degeneracy parameter of the acting electrons λ_1 is defined by equation (15). The factor $h(\lambda_1)$ is a function of λ_1 and has a form

$$h(\lambda_1) = \frac{3F_{1/2}^2(\lambda_1)}{F_{3/2}(\lambda_1)F_{-1/2}(\lambda_1)} \tag{42}$$

which has asymptotic values $h = 1$ for $\lambda_1 \ll 0$ and $h = 5/3$ for $\lambda_1 \gg 0$.

4.6. Discussion

In this section, we archive a complete algorithm for calculating the pressure and internal energy with Eqs. (30)-(42). All of the expressions have explicit and simple form although some approximations have been adopted. The first approximation is the use of one-component plasma model for Coulomb coupling in Sect. 2.1. However, it is a good approximation when the corrections from partial ionization and element mixture are added. And it is valid for a very wide range of the Coulomb coupling parameter with $0 \leq \Gamma \leq 160$. The second one is the model of pressure ionization established in Sect. 2.2. It is based on the concept of the pressure impact of acting particles on the acted-upon atom, and represents the ionization of atoms by the high pressure of matter. Its simplicity allows to retain the analytical expressions for the contribution from pressure ionization to the pressure and internal energy.

The algorithm of the EOS established in Sect.3 and 4 is based on the chemical picture for mixed elements. It allows to easily include more elements for their contribution to the EOS. The formalism for hydrogen can be developed for the elements with molecules while that for helium can be developed for the elements with multielectron atoms.

5. Results

5.1. Contribution from nonideal effects

Pressure ionization and Coulomb coupling lead to the nonideal effects on the EOS. They not only increase the ionization degrees, but also contribute to thermodynamic functions. In Sect. 4, the formalism for the EOS separates their contribution terms from those ideal terms of classical particles and free electrons. This allows to examine the importance of pressure ionization and Coulomb coupling for their contribution to the pressure and internal energy.

In spite of the reliability of our EOS for very cool-dense fluids, we performed the calculation upto very high densities for low temperatures ($T \geq 10^2 K$). That reaches the states of molecular solid and metallic solid (see Kerley 1972). The simplicity of the EOS formalism allows to easily obtain the solution and to roughly investigate the properties of matter from hot gases, to cool-dense fluids, and to solids.

We first examine the contributions from pressure ionization and Coulomb coupling to the pressure and internal energy for a H-He mixture with $X/Y = 0.7/0.3$. Their fractions over total pressure and internal energy are plotted in Fig. 3 and Fig. 4 for a $\rho - T$ domain. They are actually

formulated by $(P_{pi} + P_{cc})/P$ and $(E_{pi} + E_{cc})/E$. Equations (34), (36), (38) and (39) indicate that pressure ionization has positive contributions to the pressure and internal energy while Coulomb coupling has negative contributions to them.

Fig. 3.— The fractions of the contribution from pressure ionization and Coulomb coupling over the total pressure in a $\rho - T$ domain for a mixture

Fig. 4.— Same as Fig. 3, but over the total internal energy.

Figures 3 and 4 reveal that the contribution from pressure ionization increases the pressure P and internal E before pressure ionization takes place. In contrast, the contribution from Coulomb coupling reduces P and E when pressure ionization occurs and a great fraction of charged particles are produced. In addition, the contribution from pressure ionization dominates both pressure and internal energy in a density range of $-1 \leq \log \rho \leq 1$ for temperatures $\log T \leq 4.5$. The contribution from Coulomb coupling can reduce the pressure and internal energy by tens percent just when pressure ionization takes place at very low temperatures.

In Figs. 5 and 6 the pressure P and internal energy density $E/V\rho$ are plotted on isotherms in a density range $-2 \leq \log \rho \leq 2$ in solid lines. Together plotted in dotted lines are the ideal terms, i.e., $P - P_{pi} - P_{cc}$ and $(E - E_{pi} - E_{cc})/V\rho$ which are the pressure and internal energy excluding the contributions from pressure ionization and Coulomb coupling. From Fig. 5 and Fig. 6 we see the following points. (1) The densities of pressure ionization are located in a very narrow range. There the ideal term of free electrons increases the pressure and internal energy rapidly and

significantly. This is the result of the fast production of free electrons due to pressure ionization. (2) The contribution from pressure ionization starts to play a role and increases the pressure and internal energy far before pressure ionization takes place. This results from the interaction among atoms when they are close to each other. (3) The contribution from Coulomb coupling plays a role just after pressure ionization takes place. A great fraction of charged particles are produced and the resulted Coulomb coupling from them reduces both pressure and internal energy. (4) The increase of the pressure and internal energy by the contribution from pressure ionization before occurring of pressure ionization and the decrease by that from Coulomb coupling after occurrence of pressure ionization smooth the variation of both pressure and internal energy in the region of pressure ionization, in spite of the fact that the fast production of free electrons by pressure ionization increase the ideal pressure and internal energy steeply and significantly.

Fig. 5.— Pressure isotherms (in unit $\mathrm{dyn/cm^2}$) in solid lines, compared with those of the ideal terms in dotted lines. The isotherms are (from bottom to top): $\log T = 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0$.

Fig. 6.— Same as Fig 5 but for internal energy density isotherms (in unit erg/g).

As a result, we may conclude that the contributions from pressure ionization and Coulomb coupling smooth the variation of the pressure and internal energy in the region of pressure ionization even when pressure ionization takes place in a very narrow density range.

5.2. Comparison of the EOS

The EOS formulated in this paper has simple and explicit expressions for its practical use. However, its reliability requires comparison with the EOS data calculated by other EOS. Of many EOSs commonly used in astrophysics we choice the EOS calculated by Saumon et al. (1995) to compare our EOS. Their EOS is based on careful study of nonideal interaction and new physical treatment of partial dissociation and ionization by both pressure and temperature effects (see Saumon and Chabrier 1991,1992). They also made comparison with other EOS for a wide $\rho - T$ domain, and gave detailed discussion and analysis.

In Fig. 7 and Fig. 8 we plot the pressure and internal energy density on isotherms from our EOS and the Saumons' EOS for a pure hydrogen fluid. The difference at low density and high temperature comes from that our EOS includes the contribution from radiation while the Saumon's does not. To fit with Saumons' EOS on the internal energy density at very low temperatures, we have to ignore the zero temperature term of vibrational energy of molecular hydrogen, i.e., the term $(1/2)k\Theta_{\mathrm{v}}$ in equation (33). Comparison in the pressure in Fig. 7 shows difference mainly at low temperatures $\log T \leq 4.5$ in the density range $-1 \leq \log \rho \leq 1$. Comparison in the internal energy density in Fig. 8 also shows the difference in the same region. These differences come from the different formalisms for the models of pressure ionization and Coulomb coupling. In spite of this, both of them prove the same tendency of the pressure and internal energy from neutral fluids to ionized plasmas.

Fig. 7.— Comparison of pressure isotherms (in unit dyn/cm^2) between our EOS (solid lines) and the Saumons' EOS (circles) for a pure hydrogen fluid. The isotherms are (from bottom to top): $\log T = 2.5, 2.9, 3.3, 3.7, 4.1, 4.5, 4.9, 5.3, 5.7$.

Another distinguished difference is revealed in the internal energy isotherm at temperature $\log T = 4.5$ in Fig. 8. The difference covers a density range $-4 \leq \log \rho \leq -1$ and is specified by $\Delta \log E = 0.07$ or 17 percent. In this region our EOS results are more close to the EOS of MHD of which a difference is found with about the same amount (see Saumon et al. 1995). The difference is argued by Saumon et al. (1995) to come from a higher degree of ionization caused by the increase of the finite size of atoms with temperature and density dependence.

For higher temperatures $\log T \geq 5$, our EOS has almost the same result as Saumons' EOS in the internal energy. However, both EOSs have smaller values than the MHD EOS. This fact has been revealed by Saumon et al. 1995. This is because both EOSs do not take into account the Stark ionization while the MHD EOS does and yields higher degrees of ionization for a partially

Fig. 8.— Same as Fig. 7 but for internal energy density isotherms (in unit erg/g).

ionized gas.

6.   Conclusions

We present a single and complete algorithm of the EOS from cool-dense fluids ($T > 10^2$K) to hot gases for a H-He mixture. The physical processes of pressure ionization and Coulomb coupling are simply modeled for its validity from cool-dense fluids to hot gases and for mixed elements. This allows to archive an EOS with explicit expressions which can be easily incorporated into the modeling of stars or planets. In addition, the simple and comprehensive algorithm also allows to incorporate more physics processes or add more elements into the EOS formalism.

We show that the thermodynamic functions remain smooth even at the abrupt occurrence of pressure ionization at very low temperatures. The contributions from the Coulomb coupling and pressure ionization to the thermodynamic function compensate the effect of the rapid increase of free electrons when pressure ionization takes place. Although the quantum exchange effect of electrons is not included, the resulted algorithm produces comprehensive data of the EOS from hot gases to cool-dense fluids.

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